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(54) Title: ADDITIVES AND FUEL COMPOSITIONS			
(57) Abstract			
Dispersant, lubricity, cetane improver and/or anti-foam additives are used in combination with copolymeric ethylene flow improver additives to enhance the cold flow properties of fuel oils.			

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Additives and Fuel Compositions

This invention relates to the use of additives for improving the cold flow properties of fuel oil, for example distillate petroleum fuel such as middle distillate fuel oil boiling within the range of 110°C to 500°C.

When fuel oils are subjected to low ambient temperatures, wax may separate out from the fuel and impair the flow properties of the oil. For example, middle distillate fuels contain wax which precipitates at low temperatures to form large waxy crystals which tend to plug the small pore openings of fuel filters. This problem is particularly acute when the fuel is a diesel fuel because the nominal apertures in the fuel filter of diesel engines are typically of diameter between about 5 and 50 microns. Additives are known in the art for overcoming the above problem and are called Flow Improvers.

Such additives may act as wax crystal modifiers when blended with waxy mineral oil by modifying the shape and size of crystals of the wax therein and reducing the adhesive forces between the crystals and between the wax and the oil to permit the oil to remain fluid at a lower temperature than in the absence of the additive.

Many additives are described in the art for improving the cold-flow properties of oils, for example in the form of oil-soluble addition products or condensates that may be polymeric or monomeric and as described, for example, in US-A-3,048,479; UK-A-1,263,152; US-A-3,961,961; and EP-A-0,261,957. Some of the above additives have been and are used commercially as Cold Flow Improvers.

The art also describes Cold Flow Improvers as being usable in combination with other additives. For example, UK-A-1,112,808 describes ethylene-vinyl acetate copolymers in combination with rust inhibitors, anti-emulsifying agents, corrosion inhibitors, anti-oxidants, dispersants, dyes, dye-stabilisers, haze-inhibitors, and anti-static additives.

In this invention, it has surprisingly been found that the cold flow properties of Cold Flow Improvers such as the above-described may be further enhanced by using co-additives not hitherto known in the art to exhibit cold flow improving properties.

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Thus, a first aspect of the invention is the use of a co-additive selected from component (A) which comprises one or more of

- (a) an oil-soluble ashless dispersant/detergent comprising an amine that is acylated with a hydrocarbyl-carboxy acylating agent or that is hydrocarbylated or that is hydrocarboxylated;
- (b) an oil-soluble lubricity additive comprising an ester of a carboxylic acid and an alcohol wherein the acid has from 2 to 50 carbon atoms and the alcohol has one or more carbon atoms;
- (c) an oil-soluble nitrate or peroxy cetane improver; and
- (d) an oil-soluble petroleum fuel anti-foam comprising a silicon-based composition or a polyamine having at least one primary or secondary amino group, acylated with a carboxylic acylating agent;

said use being in a composition comprising a major proportion of a fuel oil and a minor proportion of component (B) which comprises a cold flow improver additive comprising a copolymeric ethylene flow improver, and being to enhance the cold flow properties of the composition.

The enhancement of the cold flow performance of component (B) by component (A) according to this invention can be applied to the blending of additives into a fuel oil. Thus, a second aspect of the invention is a process for blending additives with a fuel oil comprising

- (i) injecting component (B) as defined above into the fuel oil;
- (ii) injecting component (A) as defined above into the fuel oil;
- (iii) measuring the cold flow properties of the fuel oil after the injections of steps (i) and (ii); and
- (iv) adjusting the relative rate of injection of components (B) and (A) and thereby their relative proportions to take account of the results of step (iii) and to provide desired cold flow properties in the fuel oil.

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In the second aspect of this invention, the fuel oil is preferably in the form of a flowing stream wherein step (i) takes place at a first station and step (ii) takes place at a second station, though the first and second stations may be co-terminous and injection be via a common injector. The process can be automated so that a sensor can carry out step (iii), e.g. by measuring the cold filter plugging point (CFPP), and the information fed via a controller to control injection of one or both of components (B) and (A).

The invention surprisingly enables less of component (B) to be used to achieve a desired cold flow improvement performance.

The features of the invention will now be discussed in further detail.

Specifications referred to hereinafter are incorporated herein by reference.

As used in this specification the term "hydrocarbyl" refers to a group having a carbon atom directly attached to the rest of the molecule and having a hydrocarbon or predominantly hydrocarbon character. Examples include hydrocarbon groups, including aliphatic (e.g. alkyl or alkenyl), alicyclic (e.g. cycloalkyl or cycloalkenyl), aromatic, and alicyclic-substituted aromatic, and aromatic-substituted aliphatic and alicyclic groups. Aliphatic groups are advantageously saturated. These groups may contain non-hydrocarbon substituents provided their presence does not alter the predominantly hydrocarbon character of the group. Examples include keto, halo, hydroxy, nitro, cyano, alkoxy and acyl. If the hydrocarbyl group is substituted, a single (mono) substituent is preferred.

Examples of substituted hydrocarbyl groups include 2-hydroxyethyl, 3-hydroxypropyl, 4-hydroxybutyl, 2-ketopropyl, ethoxyethyl, and propoxypropyl. The groups may also or alternatively contain atoms other than carbon in a chain or ring otherwise composed of carbon atoms. Suitable hetero atoms include, for example, nitrogen, sulphur, and, preferably, oxygen.

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COMPONENT (A)

Reference is made to components as identified above by lower case code letters.

(a) ashless dispersants are dispersants for improving the detergency of fuel oils and leave little or no metal-containing residue on combustion. They are described in numerous patent specifications and include the following:

- polyamines that have been acylated with hydrocarbyl polycarboxy acylating agents (e.g. hydrocarbyl dicarboxylic anhydride) such as alkenyl succinimide polyamines, for example where the alkenyl group is polyisobutylene. Examples are described in EP-A-0,482,253. Also, included are cyclised products of such polyamines such as described in EP-A-0,525,052.
- polyamines that have been hydrocarbylated, e.g. with a polyolefin group such as polyisobutylene. Examples are described in WO 91/12302.
- hydrocarbyl ether amines such as alkyl ether monoamines, for example where the hydrocarbyl group has from 6 to 26 carbon atoms (e.g. 8 or 10) and is preferably a methyl branched alkyl such as an oxo-alcohol derivative. The amine may, for example have 2 to 8 carbon atoms. Examples are described in US-A-4,319,987. Other examples are alkoxylated amines such as described in US-A-4,409,000.

(b) The acid, alcohol and ester characterising the lubricity additive will now be discussed in further detail as follows.

(i) Acid

The acid from which the ester is derived may be a mono or polycarboxylic acid such as aliphatic, saturated or unsaturated, straight or branched chain, mono and dicarboxylic acids being preferred. For example, the acid may be generalised in the formula



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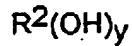
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where x represents an integer and is 1 or more such as 1 to 4, and R' represents a hydrocarbyl group having from 2 to 50 carbon atoms and which is mono or polyvalent corresponding to the value of x, the -COOH groups, when more than one is present, optionally being substituent on different carbon atoms from one another.

'Hydrocarbyl' means a group containing carbon and hydrogen which group is connected to the rest of the molecule via a carbon atom. It may be straight or branched chain which chain may be interrupted by one or more hetero atoms such as O, S, N or P, may be saturated or unsaturated, may be aliphatic or alicyclic or aromatic including heterocyclic, or may be substituted or unsubstituted. Preferably, when the acid is monocarboxylic, the hydrocarbyl group is an alkyl group or an alkenyl group having 10 (e.g. 12) to 30 carbon atoms, i.e. the acid is saturated or unsaturated. The alkenyl group may have one or more double bonds, such as 1, 2 or 3. Examples of saturated carboxylic acids are those with 10 to 22 carbon atoms such as oleic, elaidic, palmitoleic, petroselic, riconoleic, eleostearic, linoleic, linolenic, eicosanoic, galoliec, erucic and hypogaeic acids. When the acid is polycarboxylic, having for example from 2 to 4 carboxy groups, the hydrocarbyl group is preferably a substituted or unsubstituted polymethylene.

(ii) Alcohol

The alcohol from which the ester is derived may be a mono or polyhydroxy alcohol such as a trihydroxy alcohol. For example, the alcohol may be generalised in the formula



where y represents an integer and is 1 or more and R² represents a hydrocarbyl group having 1 or more carbon atoms such as up to 10 carbon atoms, and which is mono or polyvalent corresponding to the value of y, the -OH groups, when more than one is present, optionally being substituent on different carbon atoms from one another.

'Hydrocarbyl' has the same meaning as given above for the acid. For the alcohol, the hydrocarbyl group is preferably an alkyl group or a

substituted or unsubstituted polymethylene group. Examples of monohydric alcohols are lower alkyl alcohols having from 1 to 6 carbon atoms such as methyl, ethyl, propyl and butyl alcohols.

Examples of polyhydric alcohols are aliphatic, saturated or unsaturated, straight chain or branched alcohols having 2 to 10, preferably 2 to 6, more preferably 2 to 4, hydroxy groups, and having 2 to 90, preferably 2 to 30, more preferably 2 to 12, most preferably 2 to 5, carbon atoms in the molecule. As more particular examples the polyhydric alcohol may be a glycol or diol, or a trihydric alcohol such as glycerol.

(iii) The Esters

The esters may be used alone or as mixtures of one or more esters and may be composed only of carbon, hydrogen and oxygen. Preferably the ester has a molecular weight of 200 or greater, or has at least 10 carbon atoms, or has both.

Examples of esters that may be used are lower alkyl esters, such as methyl esters, of the above exemplified saturated or unsaturated monocarboxylic acids. Such esters may, for example, be obtained by saponification and esterification of natural fats and oils of plant or animal origin or by their transesterification with lower aliphatic alcohols.

Examples of esters of polyhydric alcohols that may be used are those where all of the hydroxy groups are esterified, those where not all of the hydroxy groups are esterified, and mixtures thereof. Specific examples are esters prepared from trihydric alcohols and one or more of the above-mentioned saturated or unsaturated carboxylic acids, such as glycerol monoesters and glycerol diesters, e.g. glycerol monooleate, glycerol dioleate and glycerol monostearate. Such polyhydric esters may be prepared by esterification as described in the art and/or may be commercially available.

The ester may have one or more free hydroxy groups.

Examples are described in WO-PCT/EP 94/00148.

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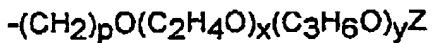
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(c) Examples of cetane improvers are organic nitrates, such as nitrate esters containing aliphatic or cyclo-aliphatic groups with up to 30 carbon atoms, preferably saturated groups, and preferably with up to 12 carbon atoms. Examples of such nitrates are methyl, ethyl, propyl, isopropyl, butyl, amyl, hexyl, heptyl, octyl, iso-octyl, 2-ethylhexyl, nonyl, decyl, allyl, cyclo-pentyl, cyclohexyl, methycyclohexyl, cyclodecyl, 2-ethoxyethyl, and 2-(2-ethoxylethoxy)ethyl nitrates. Other examples are fuel soluble peroxides, hydroperoxides and peroxy esters.

(d) Examples of anti-foams include siloxane-polyoxyalkylene copolymers, for example those described in U.S. Patent No. 3 233 986, the disclosure of which is incorporated by reference herein, which comprise at least one siloxane block containing at least two siloxane groups of the formula $R_2SiO_{0.5(4-b)}$ wherein R represents a halogen atom or an optionally halogenated hydrocarbon group and b represents from 1 to 3, and at least one polyoxylalkylene block containing at least two oxyalkylene groups. Generally, the alkylene groups have 2 or 3 carbon atoms, and usually both ethylenoxy and propyleneoxy groups are present. Advantageously, the copolymer is a polymethylsiloxane-polyoxylalkylene copolymer, preferably of the general formula



in which A represents



in which Z represents hydrocarbyl, OC(hydrocarbyl) or, preferably, hydrogen, and in which the absolute values of m and n, and their ratios, and the values of p, x, and y, and their ratios, may vary widely but total values advantageously give a weight average molecular weight in the range of from 600 to 25000. The ratio of m:n is advantageously in the range of from 10:1 to 1:20, or the value of n may be zero, and the ratio of x:y is advantageously in the range of from 1:100 to 100:1, preferably 20:80 to 100:1, or one of x or y, but not both, may be zero. Preferred foam inhibitors are those sold under the trade mark TEGOPREN by Th. Goldschmidt AG. Advantageously, the foam inhibitor is present in the fuel in a proportion in the range of from 0.0001 to 0.2% , preferably from 0.005 to 0.02%, by weight. Other anti-foams may be non-silicon containing such as those made by acylating polyamines as described in WO 94/06894.

COMPONENT (B)

Ethylene copolymer flow improvers, e.g. ethylene/unsaturated ester copolymer flow improvers have a polymethylene backbone divided into segments by oxyhydrocarbon side chains.

More especially, the copolymer may comprise an ethylene copolymer having, in addition to units derived from ethylene, units of the formula



wherein R⁶ represents hydrogen or a methyl group;

R⁵ represents a -OOCR⁸ or -COOR⁸ group wherein R⁸ represents hydrogen or a C₁ to C₂₈, preferably C₁ to C₉, straight or branched chain alkyl group, provided that R⁸ does not represent hydrogen when R⁵ represents -COOR⁸; and R⁷ is hydrogen or -COOR⁸.

These may comprise a copolymer of ethylene with an ethylenically unsaturated ester, or derivatives thereof. An example is a copolymer of ethylene with an ester of an unsaturated carboxylic acid, but the ester is preferably one of an unsaturated alcohol with a saturated carboxylic acid. An ethylene-vinyl ester copolymer is advantageous; an ethylene-vinyl acetate, ethylene vinyl propionate, ethylene-vinyl hexanoate, or ethylene-vinyl octanoate copolymer is preferred. Preferably, the copolymers contain from 1 to 25, e.g. 1 to 20 mole % of the vinyl ester, more preferably from 3 to 17 mole % vinyl ester. They may also be in the form of mixtures of two copolymers such as those described in US Patent 3,961,916. Preferably, number average molecular weight, as measured by vapour phase osmometry, of the copolymer is 1,000 to 10,000, more preferably 1,000 to 5,000. If desired, the copolymers may be derived from additional comonomers, e.g. they may be terpolymers or tetrapolymers or higher polymers, for example where the additional comonomer is isobutylene or diisobutylene.

The copolymers may be made by direct polymerisation of comonomers. Such copolymers may also be made by transesterification, or by hydrolysis and re-esterification, of an ethylene unsaturated ester copolymer to give a different ethylene unsaturated ester copolymer. For example, ethylene vinyl hexanoate and ethylene vinyl octanoate copolymers may be made in this way, e.g. from an ethylene vinyl acetate copolymer.

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Component (B) may be used with co-components such as one or more of the following:

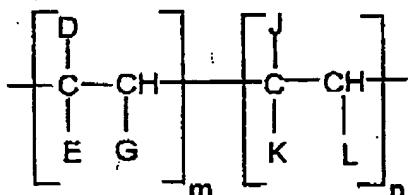
Comb Polymers

Comb polymers are discussed in "Comb-Like Polymers. Structure and Properties", N. A. Platé and V. P. Shibaev, J. Poly. Sci. Macromolecular Revs., 8, p 117 to 253 (1974).

Generally, comb polymers have one or more long chain branches such as hydrocarbyl branches, such as oxyhydrocarbyl branches, having from 10 to 30 carbon atoms, pendant from a polymer backbone, said branch or branches being bonded directly or indirectly to the backbone. Examples of indirect bonding include bonding via interposed atoms or groups, which bonding can include covalent and/or electrovalent bonding such as in a salt.

Advantageously, the comb polymer is a homopolymer having, or a copolymer at least 25 and preferably at least 40, more preferably at least 50, molar per cent of the units of which have, side chains containing at least 6, and preferably at least 10, atoms, selected from for example carbon, nitrogen and oxygen, in a linear chain.

As examples of preferred comb polymers there may be mentioned those containing units of the general formula



where D = R¹¹, COOR¹¹, OCOR¹¹, R¹²COOR¹¹ or OR¹¹
 E = H, CH₃, D or R¹²
 G = H or D
 J = H, R¹², R¹²COOR¹¹, or an aryl or heterocyclic group
 K = H, COOR¹², OCOR¹², OR¹² or COOH
 L = H, R¹², COOR¹², OCOR¹² or aryl
 R¹¹ ≥ C₁₀ hydrocarbyl
 R¹² ≥ C₁ hydrocarbyl

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and m and n represent mole ratios, their sum being 1 and m being finite and being up to and including 1 and n being from zero to less than 1, preferably m being within the range of from 1.0 to 0.4, n being in the range of from 0 to 0.6. R¹¹ advantageously represents a hydrocarbyl group with from 10 to 30 carbon atoms, and R¹² advantageously represents a hydrocarbyl group with from 1 to 30 carbon atoms.

The comb polymer may contain units derived from other monomers if desired or required. It is within the scope of the invention to include two or more different comb copolymers.

These comb polymers may be copolymers of maleic anhydride or fumaric acid and another ethylenically unsaturated monomer, e.g. an α -olefin or an unsaturated ester, for example, vinyl acetate. It is preferred but not essential that equimolar amounts of the comonomers be used although molar proportions in the range of 2 to 1 and 1 to 2 are suitable. Examples of olefins that may be copolymerized with e.g. maleic anhydride, include 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, and 1-octadecene.

The copolymer may be esterified by any suitable technique and although preferred it is not essential that the maleic anhydride or fumaric acid be at least 50% esterified. Examples of alcohols which may be used include n-decan-1-ol, n-dodecan-1-ol, n-tetradecan-1-ol, n-hexadecan-1-ol, and n-octadecan-1-ol. The alcohols may also include up to one methyl branch per chain, for example, 1-methylpentadecan-1-ol, 2-methyltridecan-1-ol. The alcohol may be a mixture of normal and single methyl branched alcohols. It is preferred to use pure alcohols rather than the commercially available alcohol mixtures but if mixtures are used the R¹² refers to the average number of carbon atoms in the alkyl group; if alcohols that contain a branch at the 1 or 2 positions are used R¹² refers to the straight chain backbone segment of the alcohol.

These comb polymers may especially be fumarate or itaconate polymers and copolymers such as for example those described in European Patent Applications 153 176, 153 177 and 225 688, and WO 91/16407.

Particularly preferred fumarate comb polymers are copolymers of alkyl fumarates and vinyl acetate, in which the alkyl groups have from 12 to 20 carbon atoms,

more especially polymers in which the alkyl groups have 14-carbon atoms or in which the alkyl groups are a mixture of C₁₄/C₁₆ alkyl groups, made, for example, by solution copolymerizing an equimolar mixture of fumaric acid and vinyl acetate and reacting the resulting copolymer with the alcohol or mixture of alcohols, which are preferably straight chain alcohols. When the mixture is used it is advantageously a 1:1 by weight mixture of normal C₁₄ and C₁₆ alcohols. Furthermore, mixtures of the C₁₄ ester with the mixed C₁₄/C₁₆ ester may advantageously be used. In such mixtures, the ratio of C₁₄ to C₁₄/C₁₆ is advantageously in the range of from 1:1 to 4:1, preferably 2:1 to 7:2, and most preferably about 3:1, by weight. The particularly preferred fumarate comb polymers may, for example, have a number average molecular weight in the range of 1,000 to 100,000, preferably 1,000 to 30,000, as measured by Vapour Phase Osmometry (VPO).

Other suitable comb polymers are the polymers and copolymers of α -olefins and esterified copolymers of styrene and maleic anhydride, and esterified copolymers of styrene and fumaric acid; mixtures of two or more comb polymers may be used in accordance with the invention and, as indicated above, such use may be advantageous.

Other examples of comb polymers are hydrocarbon polymers such as copolymers of ethylene and at least one α -olefin, preferably the α -olefin having at most 20 carbon atoms, examples being n-decene-1 and n-dodecene-1. Preferably, the number average molecular weight of such a copolymer is at least 30,000. The hydrocarbon copolymers may be prepared by methods known in the art, for example using a Ziegler type catalyst.

Linear Group Compounds

Such compounds comprise a compound in which at least one substantially linear alkyl group having 10 to 30 carbon atoms is connected to a non-polymeric organic residue to provide at least one linear chain of atoms that includes the carbon atoms of said alkyl groups and one or more non-terminal oxygen atoms.

By "substantially linear" is meant that the alkyl group is preferably straight chain, but that essentially straight chain alkyl groups having a small degree of branching such as in the form of a single methyl group may be used.

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Preferably, the compound has at least two of said alkyl groups when the linear chain may include the carbon atoms of more than one of said alkyl groups. When the compound has at least three of said alkyl groups, there may be more than one of such linear chains, which chains may overlap. The linear chain or chains may provide part of a linking group between any two such alkyl groups in the compound.

The oxygen atom or atoms are preferably directly interposed between carbon atoms in the chain and may, for example, be provided in the form of a mono- or poly-oxyalkylene group, said oxyalkylene group preferably having 2 to 4 carbon atoms, examples being oxyethylene and oxypropylene.

As indicated the chain or chains include carbon and oxygen atoms. They may also include other hetero-atoms such as nitrogen atoms.

The compound may be an ester where the alkyl groups are connected to the remainder of the compound as -O-CO n alkyl, or -CO-O n alkyl groups, in the former the alkyl groups being derived from an acid and the remainder of the compound being derived from a polyhydric alcohol and in the latter the alkyl groups being derived from an alcohol and the remainder of the compound being derived from a polycarboxylic acid. Also, the compound may be an ester where the alkyl groups are connected to the remainder of the compound as —O—n—alkyl groups. The compound may be both an ester and an ether or it may contain different ester groups.

Examples include polyoxyalkylene esters, ethers, ester/ethers and mixtures thereof, particularly those containing at least one, preferably at least two, C₁₀ to C₃₀ linear alkyl groups and a polyoxyalkylene glycol group of molecular weight up to 5,000, preferably 200 to 5,000, the alkylene group in said polyoxyalkylene glycol containing from 1 to 4 carbon atoms, as described in EP-A-61 895 and in U.S. Patent No. 4,491,455.

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The preferred esters, ethers or ester/ethers which may be used may be structurally depicted by the formula



where R^{23} and R^{24} are the same or different and may be

- (a) n-alkyl-
- (b) n-alkyl-CO-
- (c) n-alkyl-OCO-(CH₂)_n-
- (d) n-alkyl-OCO-(CH₂)_nCO-

n being, for example, 1 to 34, the alkyl group being linear and containing from 10 to 30 carbon atoms, and B representing the polyalkylene segment of the glycol in which the alkylene group has from 1 to 4 carbon atoms, for example, polyoxymethylene, polyoxyethylene or polyoxytrimethylene moiety which is substantially linear; some degree of branching with lower alkyl side chains (such as in polyoxypropylene glycol) may be tolerated but it is preferred that the glycol should be substantially linear. B may also contain nitrogen.

Suitable glycols generally are substantially linear polyethylene glycols (PEG) and polypropylene glycols (PPG) having a molecular weight of about 100 to 5,000, preferably about 200 to 2,000. Esters are preferred and fatty acids containing from 10 to 30 carbon atoms are useful for reacting with the glycols to form the ester additives, it being preferred to use C₁₈ to C₂₄ fatty acid, especially behenic acid. The esters may also be prepared by esterifying polyethoxylated fatty acids or polyethoxylated alcohols.

Polyoxyalkylene diesters, diethers, ether/esters and mixtures thereof are suitable as additives, diesters being preferred when the petroleum based component is a narrow boiling distillate, when minor amounts of monoethers and monoesters (which are often formed in the manufacturing process) may also be present. It is important for active performance that a major amount of the dialkyl compound is present. In particular, stearic or behenic diesters of polyethylene glycol, polypropylene glycol or polyethylene/polypropylene glycol mixtures are preferred.

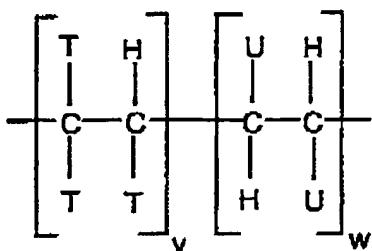
Examples of other compounds in this general category are those described in Japanese Patent Publication Nos. 2-51477 and 3-34790, and EP-A-117,108 and EP-A-326,356, and cyclic esterified ethoxylates such as described EP-A-356,256.

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Hydrocarbon Polymers

Examples are those represented by the following general formula



where $T = H$ or R^1
 $U = H, T$ or aryl
 $R^1 = C_{1-30}$ hydrocarbyl

and v and w represent mole ratios, v being within the range 1.0 to 0.0, w being within the range 0.0 to 1.0.

These polymers may be made directly from ethylenically unsaturated monomers or indirectly by hydrogenating the polymer made from monomers such as isoprene and butadiene.

Preferred hydrocarbon polymers are copolymers of ethylene and at least one α -olefin, having a number average molecular weight of at least 30,000. Preferably the α -olefin has at most 20 carbon atoms. Examples of such olefins are propylene, 1-butene, isobutene, n-octene-1, isoctene-1, n-decene-1, and n-dodecene-1. The copolymer may also comprise small amounts, e.g. up to 10% by weight of other copolymerizable monomers, for example olefins other than α -olefins, and non-conjugated dienes. The preferred copolymer is an ethylene-propylene copolymer. It is within the scope of the invention to include two or more different ethylene- α -olefin copolymers of this type.

The number average molecular weight of the ethylene- α -olefin copolymer is, as indicated above, at least 30,000, as measured by gel permeation chromatography (GPC) relative to polystyrene standards, advantageously at least 60,000 and preferably at least 80,000. Functionally no upper limit arises but difficulties of mixing result from increased viscosity at molecular weights above about 150,000, and preferred molecular weight ranges are from 60,000 and 80,000 to 120,000.

Advantageously, the copolymer has a molar ethylene content between 50 and 85 per cent. More advantageously, the ethylene content is within the range of from 57 to 80%, and preferably it is in the range from 58 to 73%; more preferably from 62 to 71%, and most preferably 65 to 70%.

Preferred ethylene- α -olefin copolymers are ethylene-propylene copolymers with a molar ethylene content of from 62 to 71% and a number average molecular weight in the range 60,000 to 120,000, especially preferred copolymers are ethylene-propylene copolymers with an ethylene content of from 62 to 71% and a molecular weight from 80,000 to 100,000.

The copolymers may be prepared by any of the methods known in the art, for example using a Ziegler type catalyst. Advantageously, the polymers are substantially amorphous, since highly crystalline polymers are relatively insoluble in fuel oil at low temperatures.

The additive composition may also comprise a further ethylene- α -olefin copolymer, advantageously with a number average molecular weight of at most 7500, advantageously from 1,000 to 6,000, and preferably from 2,000 to 5,000, as measured by vapour phase osmometry. Appropriate α -olefins are as given above, or styrene, with propylene again being preferred. Advantageously the ethylene content is from 60 to 77 molar per cent although for ethylene-propylene copolymers up to 86 molar per cent by weight ethylene may be employed with advantage.

Examples of hydrocarbon polymers are described in WO-A-9 111 488.

Polar Compounds

Such compounds comprise an oil-soluble polar nitrogen compound carrying one or more, preferably two or more, substituents of the formula =NR¹, where R¹ represents a hydrocarbyl group containing 8 to 40 atoms, which substituent or one or more of which substituents may be in the form of a cation derived therefrom. The oil-soluble polar nitrogen compound is either ionic or non-ionic and is capable of acting as a wax crystal growth inhibitor in fuels. It comprises for example one or more of the compounds (i) to (iii) as follows:

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(i) An amine salt and/or amide formed by reacting at least one molar proportion of a hydrocarbyl substituted amine with a molar proportion of a hydrocarbyl acid having 1 to 4 carboxylic acid groups or its anhydride, the substituent(s) of formula $=NR^1$ being of the formula $-NR^1R^2$ where R^1 is defined as above and R^2 represents hydrogen or R^1 , provided that R^1 and R^2 may be the same or different, said substituents constituting part of the amine salt and/or amide groups of the compound.

Ester/amides may be used containing 30 to 300, preferably 50 to 150 total carbon atoms. These nitrogen compounds are described in US Patent 4 211 534. Suitable amines are usually long chain C₁₂-C₄₀ primary, secondary, tertiary or quaternary amines or mixtures thereof but shorter chain amines may be used provided the resulting nitrogen compound is oil soluble and therefore normally contains about 30 to 300 total carbon atoms. The nitrogen compound preferably contains at least one straight chain C₈ to C₄₀, preferably C₁₄ to C₂₄, alkyl segment.

Suitable amines include primary, secondary, tertiary or quaternary, but preferably are secondary. Tertiary and quaternary amines can only form amine salts. Examples of amines include tetradecyl amine, cocoamine, and hydrogenated tallow amine. Examples of secondary amines include dioctadecyl amine and methyl-behenyl amine. Amine mixtures are also suitable such as those derived from natural materials. A preferred amine is a secondary hydrogenated tallow amine of the formula HNR¹R² wherein R¹ and R² are alkyl groups derived from hydrogenated tallow fat composed of approximately 4% C₁₄, 31% C₁₆, 59% C₁₈.

Examples of suitable carboxylic acids and their anhydrides for preparing the nitrogen compounds include cyclohexane 1,2 dicarboxylic acid, cyclohexene 1,2 dicarboxylic acid, cyclopentane 1,2 dicarboxylic acid and naphthalene dicarboxylic acid, and 1,4-dicarboxylic acids including dialkyl spirobislactone. Generally, these acids have about 5-13 carbon atoms in the cyclic moiety. Preferred acids useful in the present invention are benzene dicarboxylic acids such as phthalic acid, isophthalic acid, and terephthalic acid. Phthalic acid or its anhydride is particularly preferred. The particularly preferred compound is the amide-amine salt formed by reacting 1 molar portion of phthalic anhydride with 2 molar portions of dihydrogenated tallow amine. Another preferred compound is the diamide formed by dehydrating this amide-amine salt.

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Other examples are long chain alkyl or alkylene substituted dicarboxylic acid derivatives such as amine salts of monoamides of substituted succinic acids, examples of which are known in the art and described in US-A-4 147 520, for example. Suitable amines may be those described above.

Other examples are condensates such as described in EP-A-327,423.

(ii) A chemical compound comprising or including a cyclic ring system, the compound carrying at least two substituents of the general formula (I) below on the ring system



where A is an aliphatic hydrocarbyl group that is optionally interrupted by one or more hetero atoms and that is straight chain or branched, and R¹ and R² are the same or different and each is independently a hydrocarbyl group containing 9 to 40 carbon atoms optionally interrupted by one or more hetero atoms, the substituents being the same or different and the compound optionally being in the form of a salt thereof.

Preferably, A has from 1 to 20 carbon atoms and is preferably a methylene or polymethylene group.

As used in this specification the term "hydrocarbyl" refers to a group having a carbon atom directly attached to the rest of the molecule and having a hydrocarbon or predominantly hydrocarbon character. Examples include hydrocarbon groups, including aliphatic (e.g. alkyl or alkenyl), alicyclic (e.g. cycloalkyl or cycloalkenyl), aromatic, and alicyclic-substituted aromatic, and aromatic-substituted aliphatic and alicyclic groups. Aliphatic groups are advantageously saturated. These groups may contain non-hydrocarbon substituents provided their presence does not alter the predominantly hydrocarbon character of the group. Examples include keto, halo, hydroxy, nitro, cyano, alkoxy and acyl. If the hydrocarbyl group is substituted, a single (mono) substituent is preferred.

Examples of substituted hydrocarbyl groups include 2-hydroxyethyl, 3-hydroxypropyl, 4-hydroxybutyl, 2-ketopropyl, ethoxyethyl, and propoxypropyl. The groups may also or alternatively contain atoms other than carbon in a chain

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or ring otherwise composed of carbon atoms. Suitable hetero atoms include, for example, nitrogen, sulphur, and, preferably, oxygen.

The cyclic ring system may include homocyclic, heterocyclic, or fused polycyclic assemblies, or a system where two or more such cyclic assemblies are joined to one another and in which the cyclic assemblies may be the same or different. Where there are two or more such cyclic assemblies, the substituents of the general formula (I) may be on the same or different assemblies, preferably on the same assembly. Preferably, the or each cyclic assembly is aromatic, more preferably a benzene ring. Most preferably, the cyclic ring system is a single benzene ring when it is preferred that the substituents are in the ortho or meta positions, which benzene ring may be optionally further substituted.

The ring atoms in the cyclic assembly or assemblies are preferably carbon atoms but may for example include one or more ring N, S or O atom, in which case or cases the compound is a heterocyclic compound.

Examples of such polycyclic assemblies include

- (a) condensed benzene structures such as naphthalene, anthracene, phenanthrene, and pyrene;
- (b) condensed ring structures where none of or not all of the rings are benzene such as azulene, indene, hydroindene, fluorene, and diphenylene oxides;
- (c) rings joined "end-on" such as diphenyl;
- (d) heterocyclic compounds such as quinoline, indole, 2:3 dihydroindole, benzofuran, coumarin, isocoumarin, benzothiophen, carbazole and thiadiphenylamine;
- (e) non-aromatic or partially saturated ring systems such as decalin (i.e. decahydronaphthalene), α -pinene, cardinene, and bornylene; and
- (f) three-dimensional structures such as norbornene, bicycloheptane (i.e. norbornane), bicyclooctane, and bicyclooctene.

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Each hydrocarbyl group constituting R¹ and R² in the invention (Formula I) may for example be an alkyl or alkylene group or a mono- or poly-alkoxyalkyl group. Preferably, each hydrocarbyl group is a straight chain alkyl group. The number of carbon atoms in each hydrocarbyl group is preferably 16 to 40, more preferably 16 to 24.

Also, it is preferred that the cyclic system is substituted with only two substituents of the general formula (I) and that A is a methylene group.

Examples of salts of the chemical compounds are the acetate and the hydrochloride.

The compounds may conveniently be made by reducing the corresponding amide which may be made by reacting a secondary amine with the appropriate acid chloride; and

(iii) A condensate of long chain primary or secondary amine with a carboxylic acid-containing polymer.

Specific examples include polymers such as described in GB-A-2,121,807, FR-A-2,592,387 and DE-A-3,941,561; and also esters of telemer acid and alkanoloamines such as described in US-A-4,639,256; and the reaction product of an amine containing a branched carboxylic acid ester, an epoxide and a mono-carboxylic acid polyester such as described in US-A4,631,071.

Sulphur Carboxy Compounds

Examples are those described in EP-A-0,261,957.

FUEL OIL

The fuel oil is suitably a middle distillate fuel oil. Such distillate fuel oils generally boil within the range of about 110°C to about 500°C, e.g. 150° to about 400°C. The fuel oil can comprise atmospheric distillate or vacuum distillate, or cracked gas oil or a blend in any proportion of straight run and thermally and/or catalytically cracked distillates. The most common petroleum distillate fuels are kerosene, jet fuel, diesel fuels, heating oil and heavy fuel oils. The heating oil

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may be a straight atmospheric distillate, or it may contain minor amounts, e.g. up to 35 wt%, of vacuum gas oil or cracked gas oils or of both.

The fuel oil may be animal, vegetable or mineral oil and may also be synthetic. It may also contain additives other than those mentioned hereinbefore.

The concentration of the additive combination in the oil may for example be in the range of 1 to 5,000 ppm of additive (active ingredient) by weight per weight of fuel, such as 10 to 2000 ppm (active ingredient) by weight per weight of fuel, preferably 25 to 500 ppm, more preferably 100 to 200 ppm.

The additive should be soluble in the oil to the extent of at least 1000 ppm by weight of oil at ambient temperature. However, at least some of the additive may come out of solution near the cloud point of the oil in order to modify the wax crystals that form.

Concentrates are convenient as a means for incorporating the additive into bulk oil such as distillate fuel, which incorporation may be done by methods known in the art. The concentrates may also contain other additives as required and preferably contain from 3 to 75 wt %, more preferably 3 to 60 wt %, most preferably 10 to 50 wt % of the additives preferably in solution in oil. Examples of carrier liquid are organic solvents including hydrocarbon solvents, for example petroleum fractions such as naphtha, kerosene and heater oil; aromatic hydrocarbon containing aromatic fractions (e.g. Solvesso (trade name)); and paraffinic hydrocarbons such as hexane, pentane and isoparaffins, and includes mixtures of the above. The carrier liquid must, of course, be selected having regard to its compatibility with the additive and with the fuel.

The additives of the invention may be incorporated into bulk oil by other methods such as those known in the art. If others are required, they may be incorporated into the bulk oil at the same time as the additives of the invention or at a different time. Examples of other additives include antioxidants, corrosion inhibitors, dehazers, metal deactivators, cosolvents, package compatibilisers, reodorants, antistatic additives (conductivity improvers), biocides, dyes, smoke reducers, catalyst life enhancers, power boosters, additives for fuel economy, demulsifiers, and spray modifiers.

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EXAMPLES

The following examples illustrate the invention.

Additives

The following additives were used, identified by their preceding reference codes:

- B1: an ethylene-vinyl acetate copolymer of number average molecular weight 3,300 as measured by Gel Permeation Chromatography (GPC) and containing about 36% by weight of vinyl acetate.
- B2: an ethylene-vinyl acetate copolymer of number average molecular weight 5,000 as measured by GPC and containing about 13.5% by weight of vinyl acetate.
- B3: a mixture of additives B1 and B2 in the weight:weight ratio (B1:B2) of 3:1.
- A1: a commercial mixture of polyethylene amines which includes penta ethylene hexamine [$\text{NH}_2(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}_2$] and tetraethylene pentamine that has been acylated with a polyisobutylene (molecular weight 950) substituted succinic anhydride to produce a polyisobutylene succinic anhydride-polyamine product.
- A2: a macrocyclic product obtained by reacting a polyisobutylene (molecular weight 950) substituted succinic anhydride with a polyamine of the formula $\text{NH}_2(\text{CH}_2)_3\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{NH}_2$ to give an acylated polyamine which is then cyclised as described in EP-A-525,052.
- A3: an ether amine of the formula R-O-(CH_2)₃NH₂ where R represents one or more iso-C₁₀ alkyl groups; as described in US-A-4,319,987.
- A4: an octyl nitrate cetane improver as known in the art and as commercially available.
- A5: an ester obtained by reacting dilinoleic acid (a C₃₆ dimer acid) with ethylene glycol and neutralising acid groups with methanol, as described in US-A-3,287,273.

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A6: ethoxylated cocoamine, sold commercially as ARMAK 1282.

A7: the product formed by reacting one mole of $\text{NH}_2(\text{C}_2\text{H}_4)\text{NH}(\text{C}_2\text{H}_4)\text{OH}$ with slightly in excess of two moles of a mixture of two linear alkanoic acids having 12 and 14 carbon atoms respectively, as described in WO 94/06894.

C: a N,N-dialkylammonium salt of 2-N¹,N¹-dialkyl-amido benzoate, being the reaction product of reacting one mole of phthalic anhydride with two moles of dihydrogenated tallow amine to form a half amide/half amine salt.

Fuels

The following fuels were used, characterised as follows:

	I	II
IBP	207	174
10%	236	220
20%	248	232
50%	281	276
70%	305	307
90%	343	346
FBP	374	369
CP	2	-3
CFPP	-4	-4
SFPP	0	-3

KEY

- All figures are in °C
- Distillation characteristics are measured according to ASTM D-86 (IBP and FBP are initial and final boiling points respectively)
- CP is Cloud Point measured according to IP 219/82
- CFPP is Cold Filter Plugging Point and SFPP is Simulated Filter Plugging Point (see below under 'TESTS' for further details)

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Tests

Additives were dissolved in the fuels and the following tests performed on fuel treated with additives to measure the following in order to assess the effectiveness of the additives tested as filterability improvers in distillate fuels.

Simulated Filter Plugging Point (SFPP)

The test was carried out by the procedure substantially as described in EP-A-0,403,097 and is a variation of the CFPP test.

The Cold Filter Plugging Point Test (or CFPP Test)

The test which is carried out by the procedure described in detail in "Journal of the Institute of Petroleum", Volume 52, Number 510, June 1966, pp. 173-285, is designed to correlate with the cold flow of a middle distillate in automotive diesels.

In brief, a sample of the oil to be tested (40 ml) is cooled in a bath which is maintained at about -34°C to give non-linear cooling at about 1°C/min. Periodically (at each one degree centigrade starting from above the cloud point), the cooled oil tested for its ability to flow through a fine screen in a prescribed time period using a test device which is a pipette to whose lower end is attached an inverted funnel which is positioned below the surface of the oil to be tested. Stretched across the mouth of the funnel is a 350 mesh screen having an area defined by a 12 millimetre diameter. The periodic tests are each initiated by applying a vacuum to the upper end of the pipette whereby oil is drawn through the screen up into the pipette to a mark indicating 20 ml of oil. After each successful passage, the oil is returned immediately to the CFPP tube. The test is repeated with each one degree drop in temperature until the oil fails to fill the pipette within 60 seconds, the temperature at which failure occurs being reported as the CFPP temperature.

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ResultsKEY

- $\Delta SFPP$ and $\Delta CFPP$ represent the difference between the SFPP (or CFPP) of the base fuel and that of the treated fuel
- The figures under the component codes are treat rates of active ingredient in parts per million per weight of fuel
- * represent results for additive combination of the invention
- a dash means that no readings were taken

FUEL I

(I)	B1	A1	A2	A6	A7	$\Delta CFPP$	$\Delta SFPP$
	60					-3	1
	100					-2	-1
		100				-0.5	0
	60	40				1	1 *
			100			0.5	1
	60		40			13	10 *
				100		-2	-
	60			40		3	- *
					100	-3.5	-2
	60				40	3	5 *
(ii)	B2	A1	A2	A5		$\Delta CFPP$	$\Delta SFPP$
	60					3	0
	100					1.5	0
		100				-0.5	0
	60	40				12	9 *
			100			0.5	1
	60		40			12	4 *
				100		3.5	0
	60				40	7	3 *

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(iii)	B3	A1	A2	$\Delta CFPP$	$\Delta SFPP$
	60			7	6
	100			9	6
		100		-0.5	0
	60	40		12	10 *
			100	0.5	1
	60		40	12	10 *

FUEL II

(i)	B1	A3	A4	$\Delta SFPP$
	180			3
	300			9
		300		-1
	180	120		8 *
			300	-1
	180		120	7 *

The results show that substituting part of the 'B' component with an 'A' component either enhances or does not deleteriously effect the filterability of the fuel. Also, they show that a filterability target can be met by the inventive combinations using less of the 'B' component, noting that the 'A' component itself provides advantageous properties.

The additive combinations of the invention may also be effective in reducing the tendency of wax in the fuel to settle (i.e. they may be wax anti-settling additives) and may exhibit activity in slow cooling tests such as the Extended Programmed Cooling Test (XPCT) which is known in the art.

FURTHER EXAMPLE

Components BX and BY were used having the following formulations respectively:

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BX: B2 (56 ppm)
B1 (169 ppm)
7 (75 ppm)
C (75 ppm)

BY: B2 (50 ppm)
3 (100 ppm)
6 (100 ppm)
C (100 ppm)
5 (200 ppm)

The concentrations of the constituents of Components BX and BY in the fuels in the tests to be described hereinafter are given in parentheses as weight per cent of fuel. The constituents, identified by reference numbers 3 and 5 to 7 above, are as follows (additional to constituents already defined herein)

- 3: an ethylene-vinyl acetate copolymer of number average molecular weight of 3,300 as measured by GPC and containing 36% by weight of vinyl acetate.
- 5: an itaconate polymer of number average molecular weight about 4000 as measured by GPC prepared by polymerising a monomer in cyclohexane solvent using a free radical catalyst, the monomer containing linear alkyl groups of 18 carbon atoms.
- 6: a copolymer of styrene and esterified fumaric acid wherein the alkyl groups have 14 carbon atoms, the copolymer having a number average molecular weight of 15000 as measured by GPC and proportions of styrene and esterified fumaric acid in the ratio of 1:1 (mole:mole).
- 7: a fumarate ester vinyl acetate copolymer of number average molecular weight of about 20,000 as measured by GPC, the fumarate ester containing linear alkyl groups of 12-14 carbon atoms.

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Component AY having the formulation consisting of the following was also used:

- a polyaminated polyisobutylene succinic anhydride detergent (200 ppm)
- an octyl nitrate cetane improver (240 ppm)
- an ethoxylated nonyl phenol antirust (20 ppm)
- a silicon-containing anti-foam (12.5 ppm)
- a reodorant (80 ppm)
- isodecanol (47.5 ppm)
- "Solvesso" 150 (385 ppm) - an aromatic diluent
- a first demulsifier (5 ppm)
- a second demulsifier (10 ppm)

The concentrations of the constituents of Component AY in the fuels in the tests to be described hereinafter are given in parentheses as weight per weight of fuel.

FUELS

The following fuels were used:

D86	IBP	165.3	155.9
Distillation (°C)	5%	192.2	185.2
	10%	196.7	189.2
	20%	207.8	200.1
	30%	218.6	210.1
	40%	231.1	222.2
	50%	246.2	236.5
	60%	263.3	253.1
	70%	283.1	273.7
	80%	306.5	301.2
	90%	333.1	334.0
	95%	349.8	354.6
	FBP	364.8	377.0

KEY

ASTM D-86

FBP, IBP are final and initial boiling points

CP as measured by IP 219/82

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Results

The results of SFPP tests are shown in the table below.

Fuel	Additive	SFPP (°C)	SFPP (°C) Diff
1	(BX)	-13	4
	(BX) + (AY)	-17	
1	(BY)	-10	5
	(BY) + (AY)	-15	
2	(BX)	-14	1
	(BX) + (AY)	-15	
2	(BY)	-13	8
	(BY) + (AY)	-21	

SFPP diff. is the difference between the SFPP obtained when Component BX (or BY) alone was used and that obtained when Component BX (or BY) and Component AY were used together. The results show that Component AY enhanced SFPP in three out of four cases.

CLAIMS

1. The use of a co-additive selected from component (A) which comprises one or more of
 - (a) an oil-soluble ashless dispersant/detergent comprising an amine that is acylated with a hydrocarbyl-carboxy acylating agent or that is hydrocarbylated or that is hydrocarboxylated;
 - (b) an oil-soluble lubricity additive comprising an ester of a carboxylic acid and an alcohol wherein the acid has from 2 to 50 carbon atoms and the alcohol has one or more carbon atoms;
 - (c) an oil-soluble nitrate or peroxy cetane improver; and
 - (d) an oil-soluble petroleum fuel anti-foam comprising a silicon-based composition or a polyamine having at least one primary or secondary amino group, acylated with a carboxylic acylating agent;said use being in a composition comprising a major proportion of a fuel oil and a minor proportion of component (B) which comprises a cold flow improver additive comprising a copolymeric ethylene flow improver, and being to enhance the cold flow properties of the composition.
2. The use of claim 1 wherein component (A) comprises a polyamine acylated with a hydrocarbyl polycarboxy acylating agent.
3. The use of claim 2 wherein component (A) comprises an alkenyl succinimide polyamine.
4. The use of claim 3 wherein the alkenyl group is polyisobutylene.
5. The use of any of the preceding claims wherein component (A) comprises an ester of a trihydric alcohol and one or more saturated or unsaturated carboxylic acids.
6. The use of claim 5 wherein the ester is glycerol monooleate.

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7. The use of any of the preceding claims wherein component (A) comprises octyl nitrate.
8. The use of any of the preceding claims component (B) comprises an ethylene/unsaturated ester copolymer.
9. The use of claim 8 wherein the unsaturated ester is of an unsaturated alcohol with a saturated carboxylic acid.
10. The use of any of the preceding claims additionally comprising, as a co-additive, an oil-soluble polar nitrogen compound carrying one or more substituents of the formula -NR¹- where R¹ represents a hydrocarbyl group containing 8 to 40 carbon atoms, which substituent or one or more of which substituents is optionally in the form of a cation derived therefrom.
11. The use of any of the preceding claims wherein the fuel oil is a middle distillate fuel oil.
12. The use of any of the preceding claims wherein the total concentration of components (A) and (B) in the fuel oil is in the range of 25 to 500 ppm of active ingredient by weight per weight of fuel oil.
13. A process for blending additives with a fuel oil comprising
 - (i) injecting component (B) as defined in claim 1 into the fuel oil;
 - (ii) injecting component (A) as defined in claim 1 into the fuel oil;
 - (iii) measuring the cold flow properties of the fuel oil after the injections of steps (i) and (ii); and
 - (iv) adjusting the relative rates of injection of components (B) and (A) and thereby their relative proportions to take account of the results of step (iii) and to provide desired cold flow properties in the fuel oil.
14. The process of claim 13 wherein the fuel oil comprises a flowing stream thereof, step (i) taking place at a first station and step (ii) taking place at a second station.

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15. The process of claim 13 or 14 wherein a sensor carries out step (iii) and information is fed via a controller to control injection of one of both of components (B) and (A).

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C10L1/14 C10L1/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR,A,1 405 551 (ESSO) 31 May 1965 see page 1, column 2 see page 3, column 1	1,5,6, 11,12
X	EP,A,0 476 196 (ETHYL) 25 March 1992 see page 10, line 37 - line 46 see page 11, line 16 - line 24; claim 4	1-4,7-9, 11,12
X	US,A,4 365 973 (IRISH) 28 December 1982	1,7-9, 11,12
Y	see the whole document	10
Y	EP,A,0 465 042 (EXXON) 8 January 1992 see the whole document	10
		-/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

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X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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A document member of the same patent family

Date of the actual completion of the international search

14 December 1994

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C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB,A,1 413 323 (UNITED LUBRICANTS) 12 November 1975 see the whole document ----	1,8,11, 12
X	EP,A,0 055 355 (BASF) 7 July 1982 see page 6, line 4 - line 11 ----	1,8,9, 11,12
P,X	WO,A,94 06894 (EXXON) 31 March 1994 cited in the application see the whole document ----	1,8-12
X	EP,A,0 030 099 (EXXON) 10 June 1981 see page 13, paragraph 2; claims 1-21 ----	1,8-12
X	FR,A,2 197 062 (ESSO) 22 March 1974 see the whole document ----	1,8,9, 11,12
A	US,A,5 018 645 (ZINSMEYER) 28 May 1991 see the whole document ----	13-15
A	EP,A,0 017 308 (THE ASSOCIATED OCTEL) 15 October 1980 see the whole document ----	13-15

information on parent family members

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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
FR-A-1405551		DE-A- 1594420 GB-A- 1065398 US-A- 3273981		23-07-70
EP-A-0476196	25-03-92	AU-B- 635158 AU-A- 8465091 CA-A- 2051452 DE-D- 69004692 DE-T- 69004692 JP-A- 4234489		11-03-93 26-03-92 21-03-92 23-12-93 10-03-94 24-08-92
US-A-4365973	28-12-82	NONE		
EP-A-0465042	08-01-92	US-A- 5094666 US-A- 5092908 CA-A- 2042855 JP-A- 4226192		10-03-92 03-03-92 29-12-91 14-08-92
GB-A-1413323	12-11-75	NONE		
EP-A-0055355	07-07-82	DE-A- 3049553		29-07-82
WO-A-9406894	31-03-94	AU-B- 4818593		12-04-94
EP-A-0030099	10-06-81	AT-T- 7151 CA-A- 1165121 JP-C- 1721334 JP-B- 2033756 JP-A- 56092996 SU-A- 1271375 US-A- 4375973 US-A- 4546137		15-05-84 10-04-84 24-12-92 30-07-90 28-07-81 15-11-86 08-03-83 08-10-85
FR-A-2197062	22-03-74	AU-A- 5846573 BE-A- 803952 CA-A- 1017568 DE-A, C 2339175 GB-A- 1436793 JP-C- 1194522 JP-A- 49063702		30-01-75 25-02-74 20-09-77 07-03-74 26-05-76 12-03-84 20-06-74

Information on patent family members

PCT/EP 94/02432

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
FR-A-2197062		JP-B- 58024477		21-05-83
		JP-C- 1448107		11-07-88
		JP-A- 58132086		06-08-83
		JP-B- 62008477		23-02-87
		NL-A- 8802850		01-03-89
		NL-A- 8802851		01-03-89
		NL-A- 7311628		26-02-74
		US-A- 3910776		07-10-75
US-A-5018645	28-05-91	DE-A- 4102456		01-08-91
		FR-A- 2657598		02-08-91
		GB-A, B 2240320		31-07-91
		JP-A- 4215997		06-08-92
		SE-A- 9100217		31-07-91
		US-A- 5163586		17-11-92
EP-A-0017308	15-10-80	FR-A- 2448130		29-08-80
		AT-T- 4253		15-08-83
		AU-B- 528960		19-05-83
		AU-A- 5472980		14-08-80
		JP-A- 55108012		19-08-80
		DA-A- 6457		31-07-81
		US-A- 4320775		23-03-82